Study of Ion-pairing and Ion Solvation in Lithium Battery Electrolytes using soft X-ray Absorption and Emission Spectroscopy

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Outline

- Motivation and Scientific issues
- Approach
- Results
- Conclusions

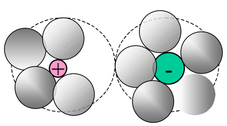
Motivation

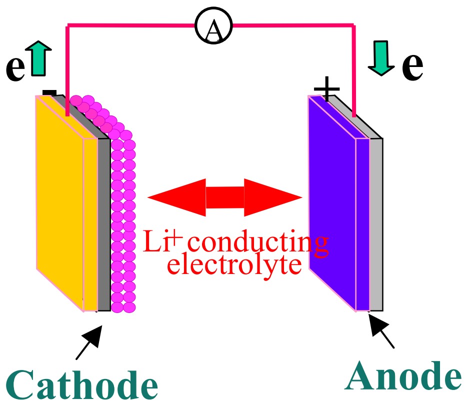
- **Rechargeable Li-ion batteries offer high energy density, flexible and light weight design**
  - ***Considered by DOE for application in all-electric vehicles (EV) and hybrid electric vehicles (HEV)***
  - ***Power source in commercial portable, entertainment, computing and telecommunication equipment***
- **Ion-pairing and ion-solvation are of fundamental interests in electrochemisty and great technological importance in Li battery**

Solvent-separated ion pair with solvation shells

Solvent-separated ion pair with sharing of solvation shells

Contact ion pair with residual solvation of the pair dipole





Scientific issues

- **Solid and liquid electrolytes in state-of-art Li-ion batteries consist of mixture of two or more aprotic solvents and Li salt**

  Solid electrolyte: polyethylene oxide (PEO), Li salt liquid electrolyte:

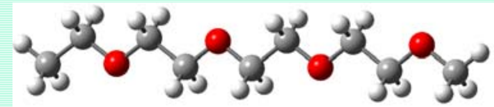
  propylene carbonate (PC), lithium bis(oxalato)borate (LiBOB)
  ethylene carbonate(EC), diethylcarbonate (DEC), $LiPF_6$

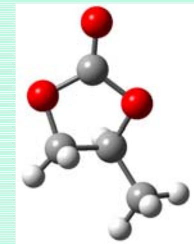
- **Electrolytes serve as medium for the transfer of charges in batteries**

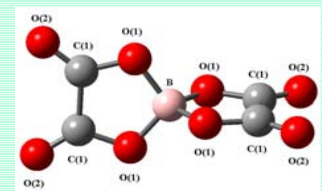
  $\sigma = \sigma_{(a)} + \sigma_{(c)}$, where $\sigma = n_{a(c)}\, \mu_{a(c)} Z_{a(c)}$

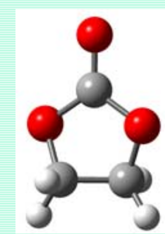
  ionic conductivity in electrolyte limited by
  a) degree of dissociation of salt
  b) mobility of solvated ions

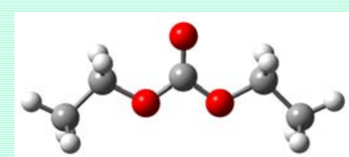
- **Solvent co-intercalation with Li^+ into graphite anode : related to ion solvation (EC vs. PC)**


PEO


PC


BOB anion


EC


DEC

Approach

Experiment: XAS, XES and RIXS

Photon-in, photon-out technique applicable to solid-
solid- liquid interface, liquid phase --- potential for in-situ
situ
electrochemistry experiments

Not limited to conducting samples--Li^+ conductors
conductors are not necessary electric
conducting

Theory: in collaboration with Prof. Yi Luo, KTH, Sweden

ab-initio HF and DFT calculation
generalized group theory formulation

Systems Studied

- **Cation-anion interaction**

  alkali salts having cation vary

  M_2CO_3, where M= Li, Na, K, Cs

  $CaCO_3$

  Li salts having anions vary

  Li_2CO_3 , $Li_2C_2O_4$, LiBOB

- **Li salt and its acid derivative**

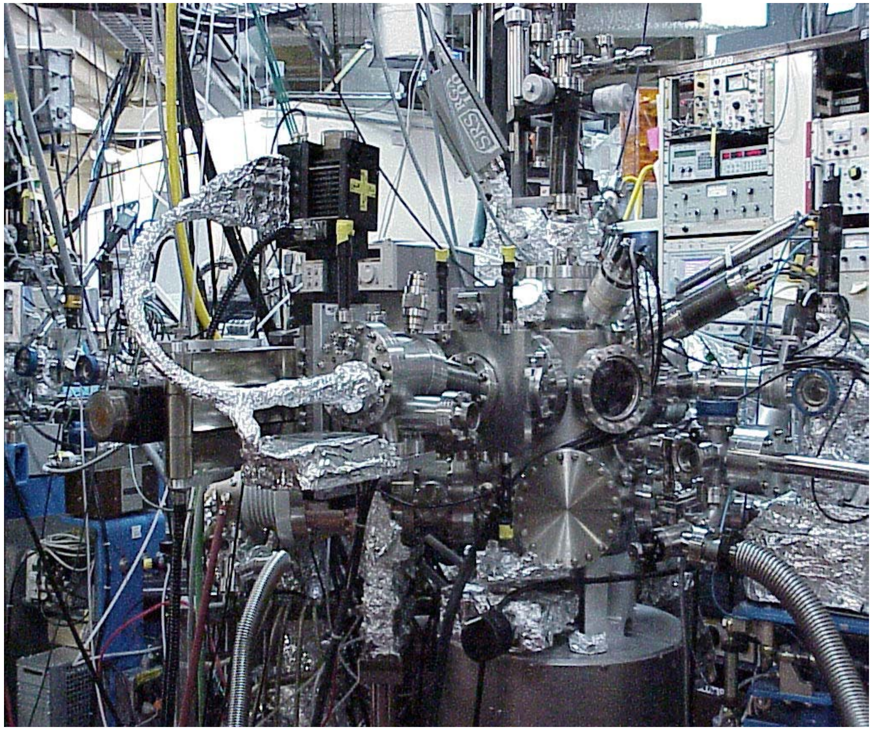
  oxalic acid, lithium oxalate; lithium succinate, succinic acid

- **Electrolyte component (PEO), electrolyte PEO-LiX**

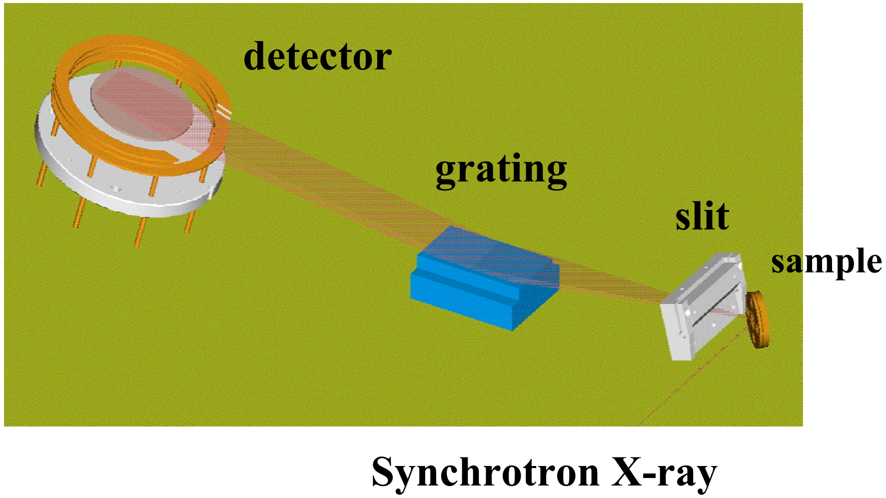
  PEO with varying molecular weight (Wt. ranging from 1000

  1000 –600,000) form (powder and film), w/wt salt PEO-LiX

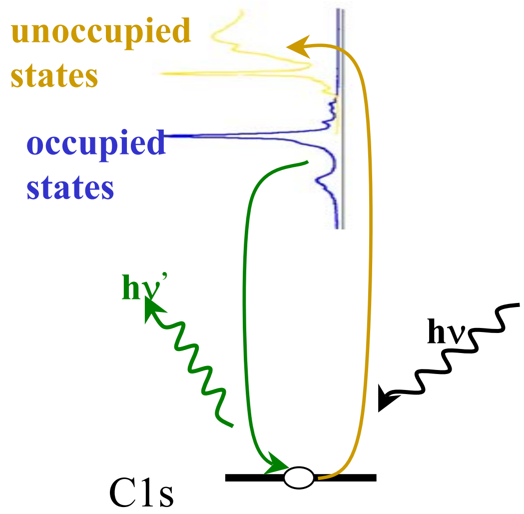
Experimental Setup

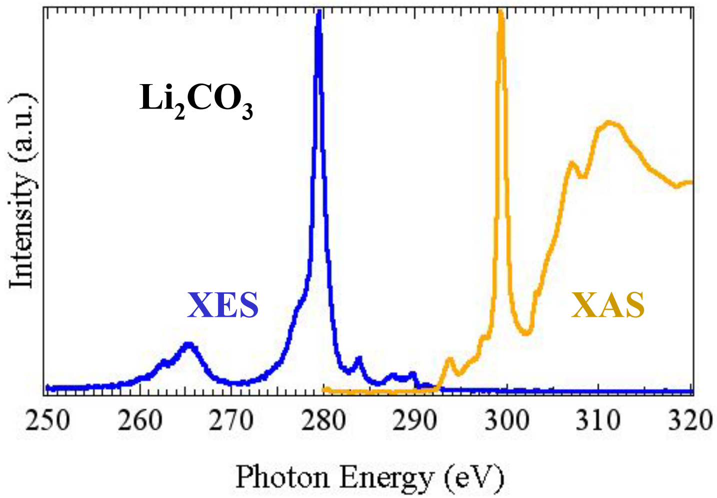


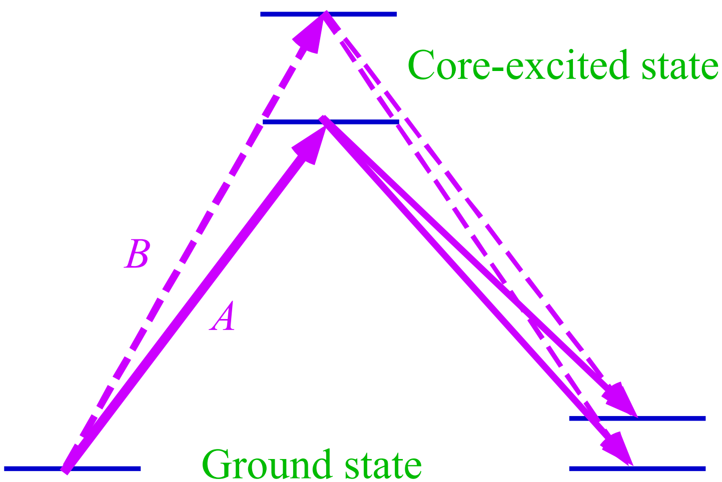
- Tunable X-ray source
- Energy range (100 eV-1000 eV) inaccessible by lab source
- High Brightness



XAS and XES and RIXS processes in a nut shell



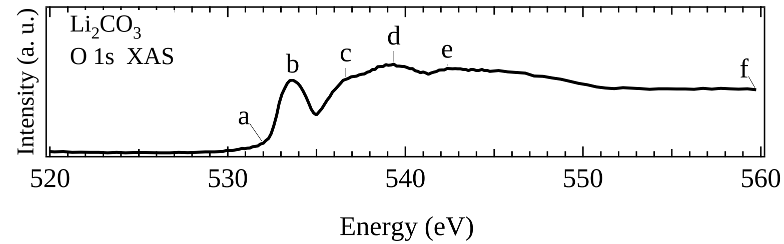


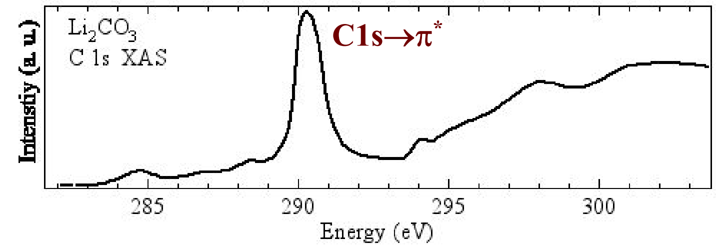


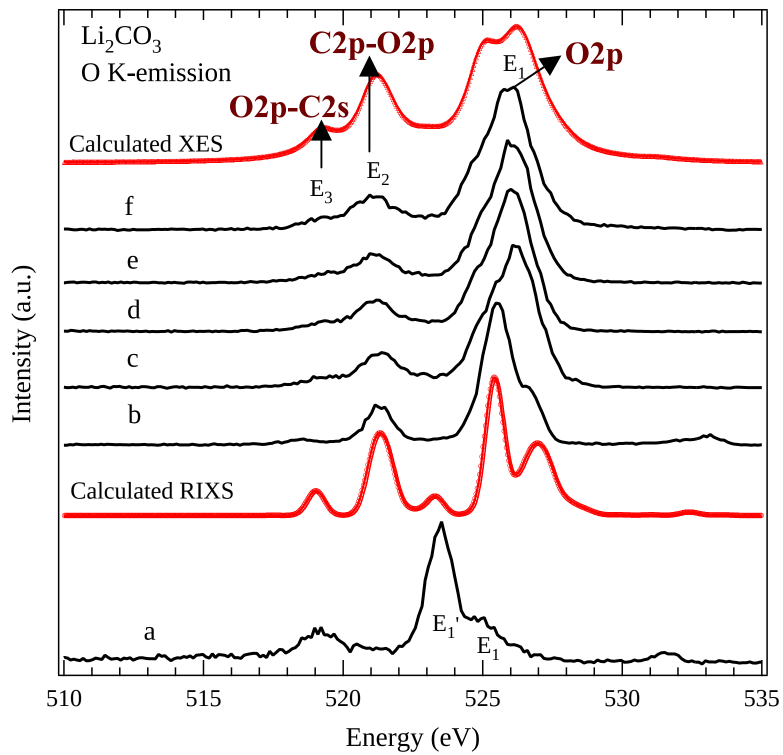
•**Basic features:**

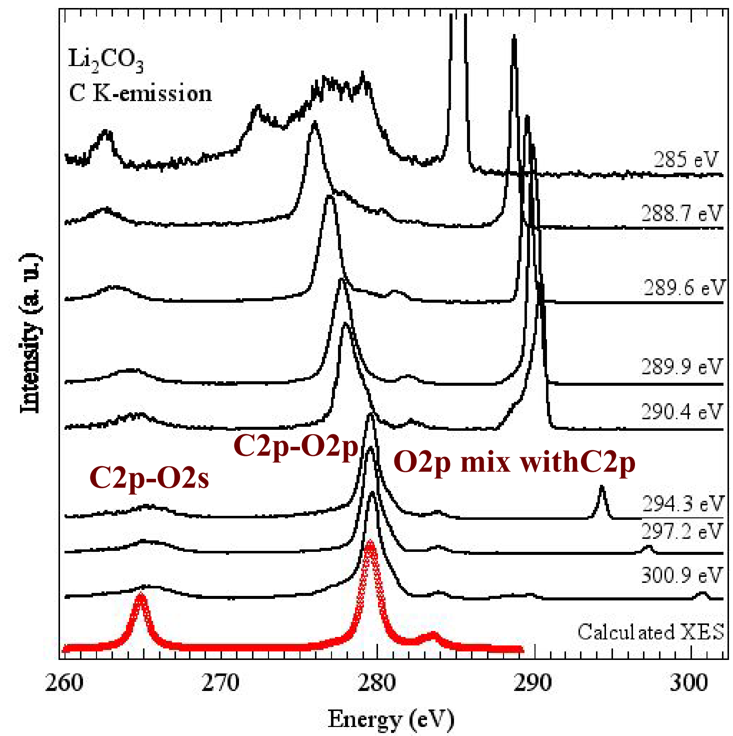
- –Elemental selectivity
- –Chemical sensitivity
- –Bulk sensitivity
- –Site selectivity

Lithium Carbonate (Li_2CO_3) — co-existing of localized and delocalized bonds

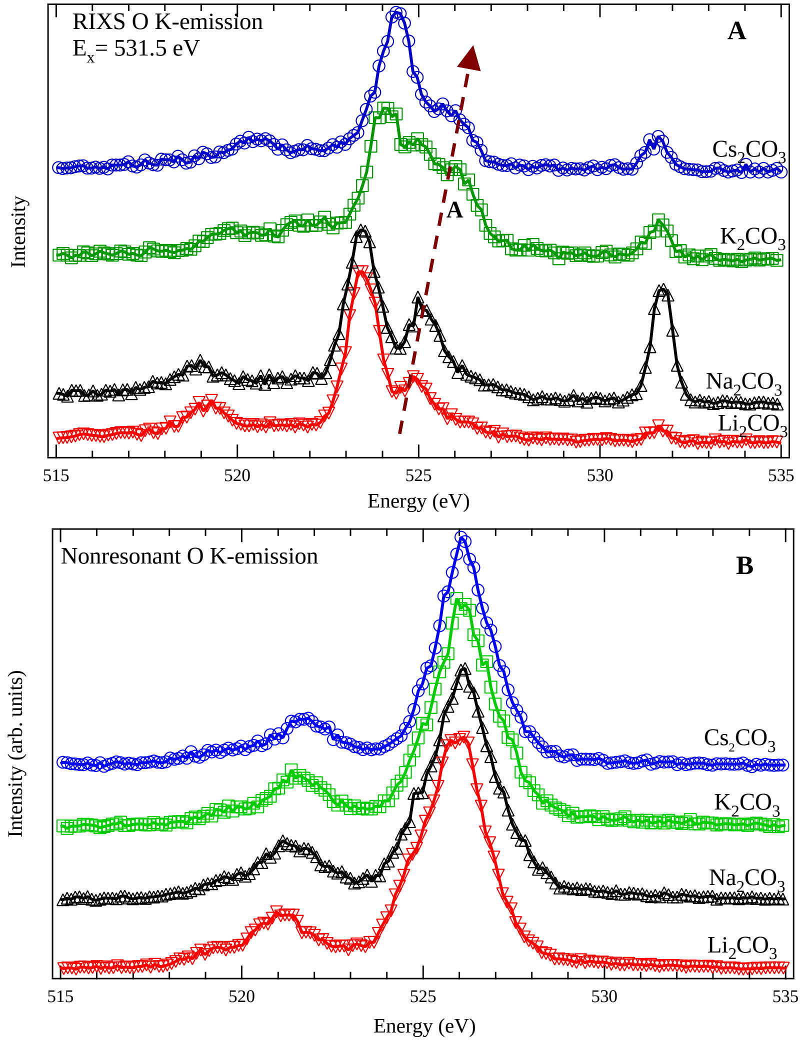


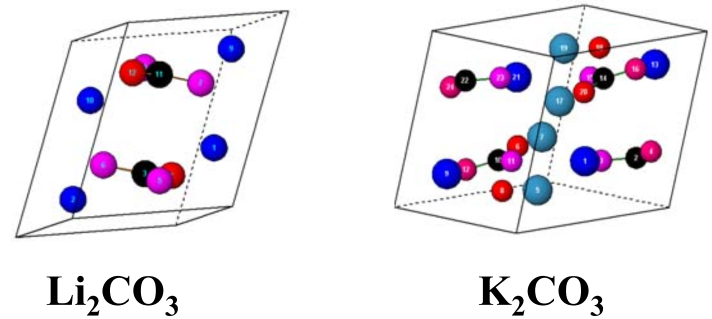


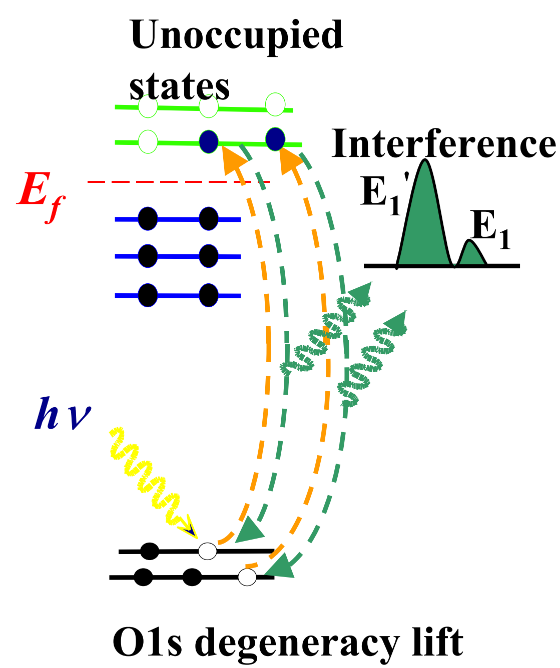




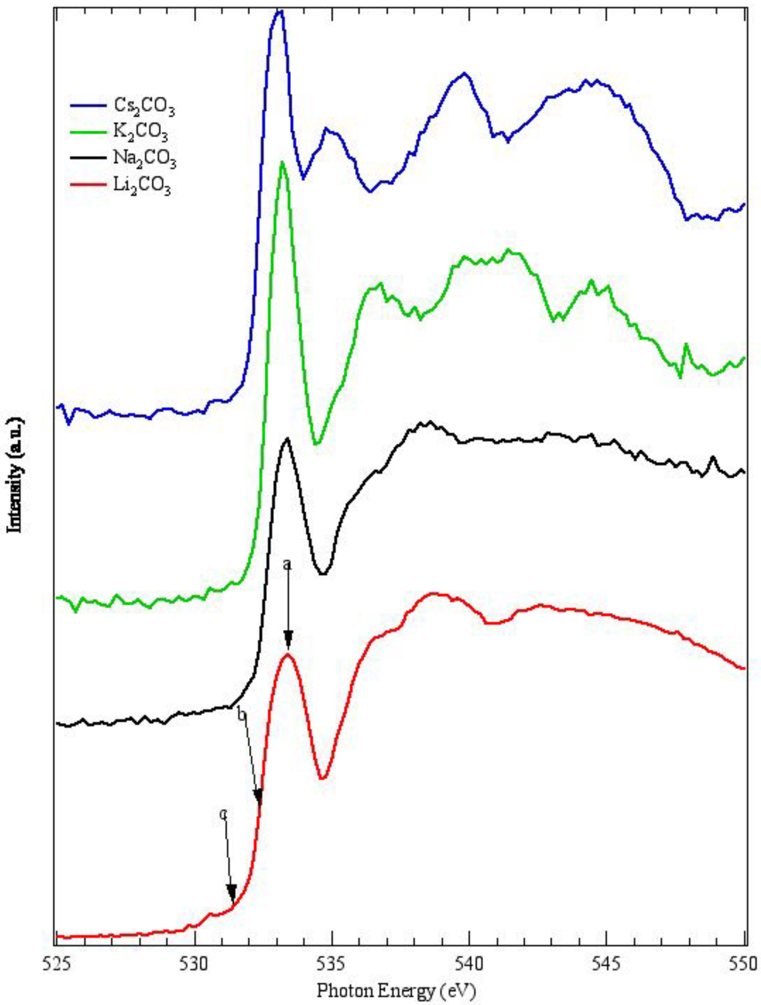
Alkali Carbonate (Li, Na, K, Cs) — ion packing on localized and delocalized bonds



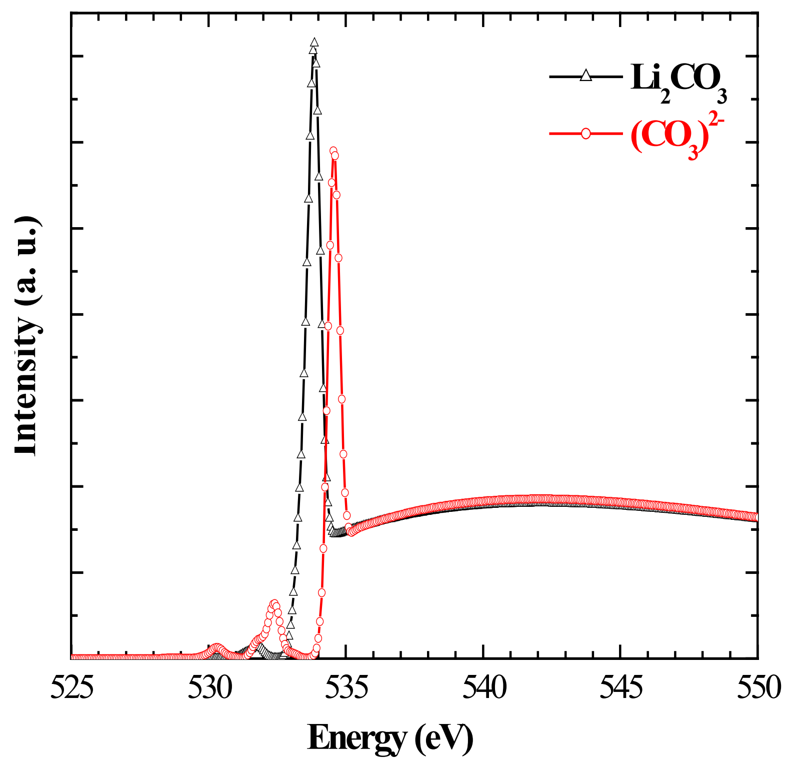




O 1s XAS

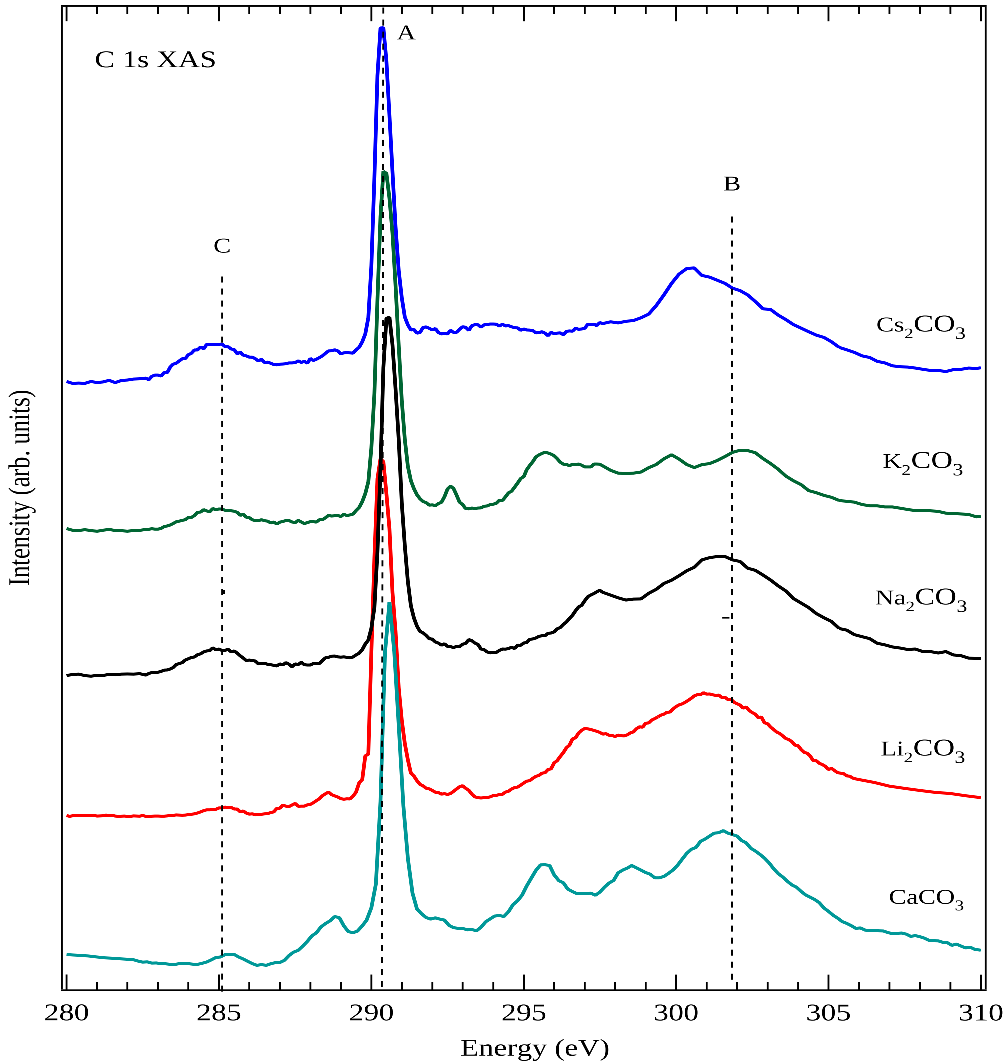


Calculation



❖Unoccupied states have extended orbitals , very sensitive to delocalized bond

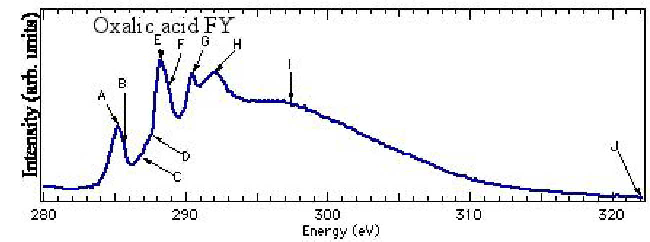
❖O π^* resonance strength suppression is a measure of charge donation from cation

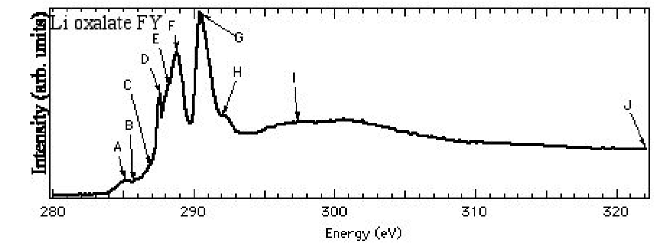


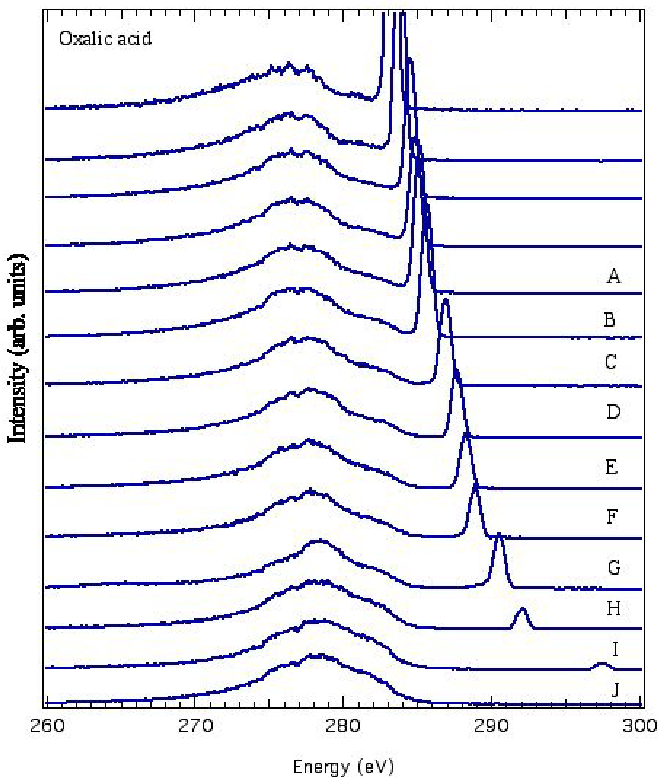
Carbon π^* (peak A)in XAS is less sensitive to the cations than Oxygen π^* Resonance

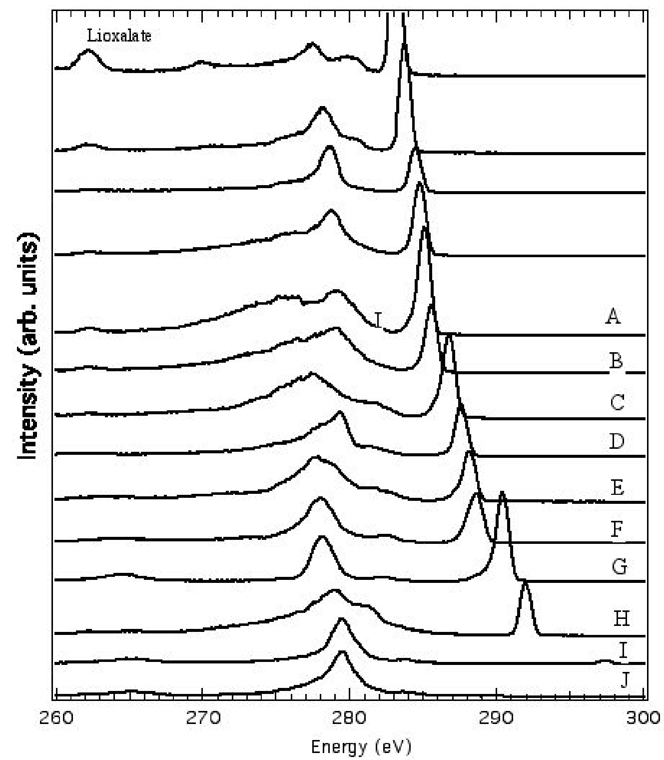
Pre-peak (C) common to all the carbonates

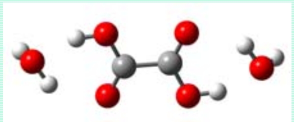
Oxalic acid vs. Lithium oxalate





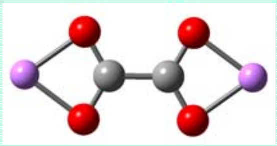






Oxalic acid

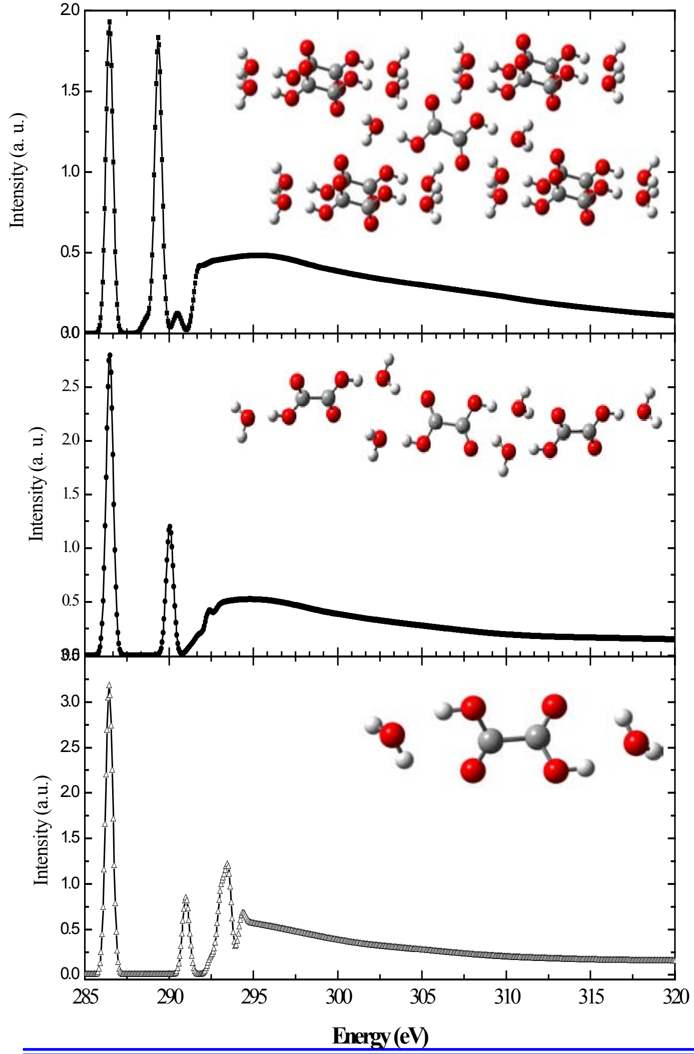
$H_2C_2O_4 \cdot 2H_2O$

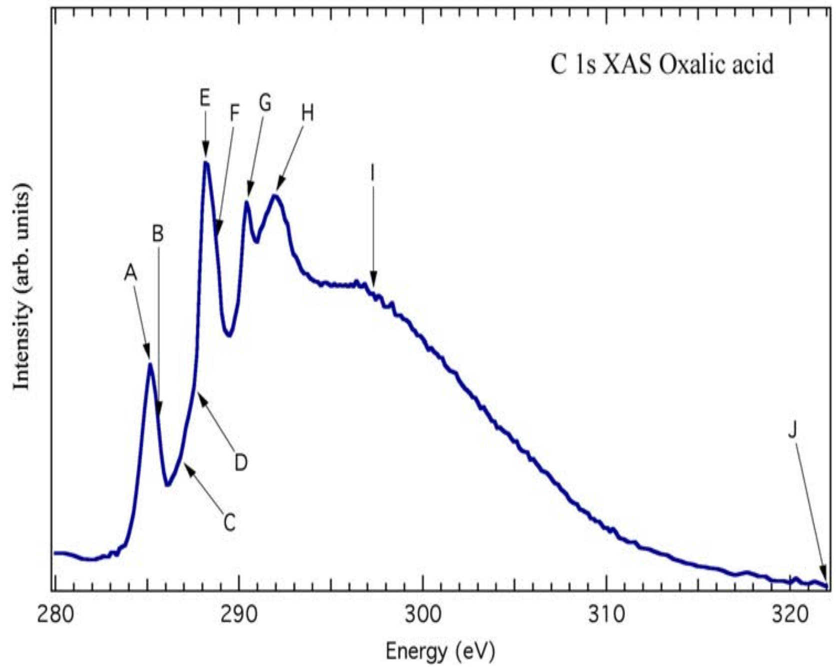


Lithium oxalate

$Li_2C_2O_4$

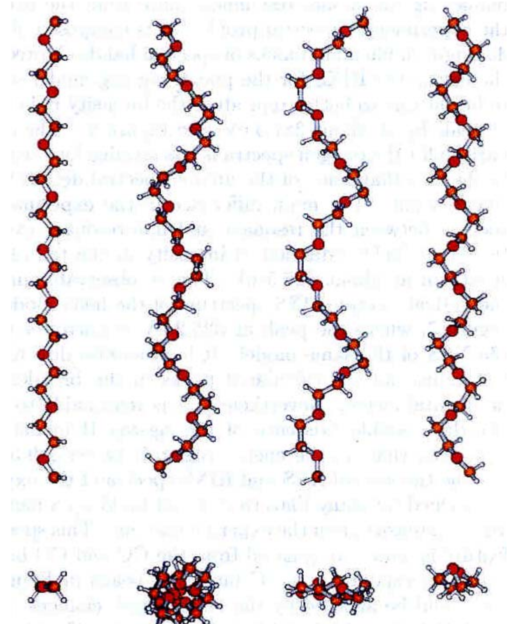
Calculated C1s XAS of oxalic acid



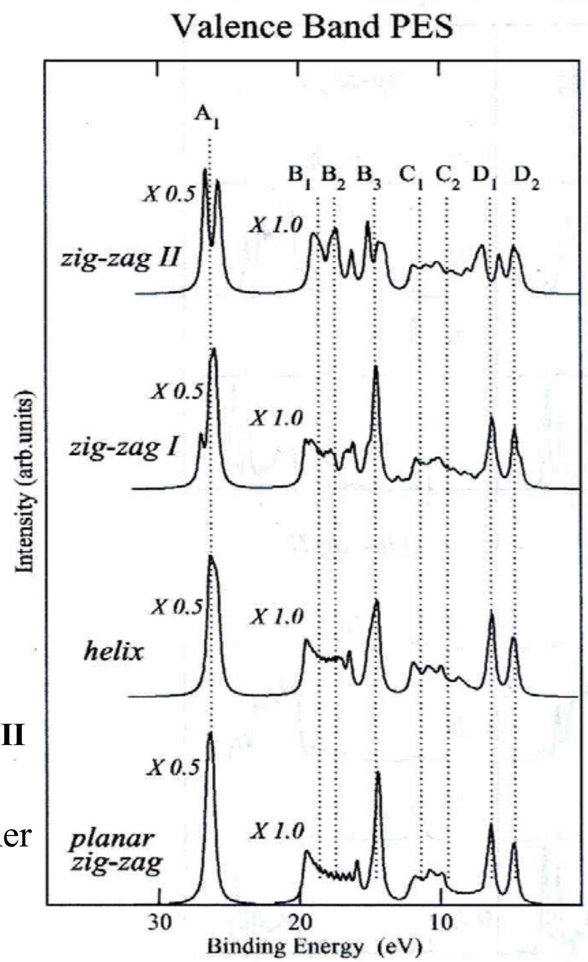


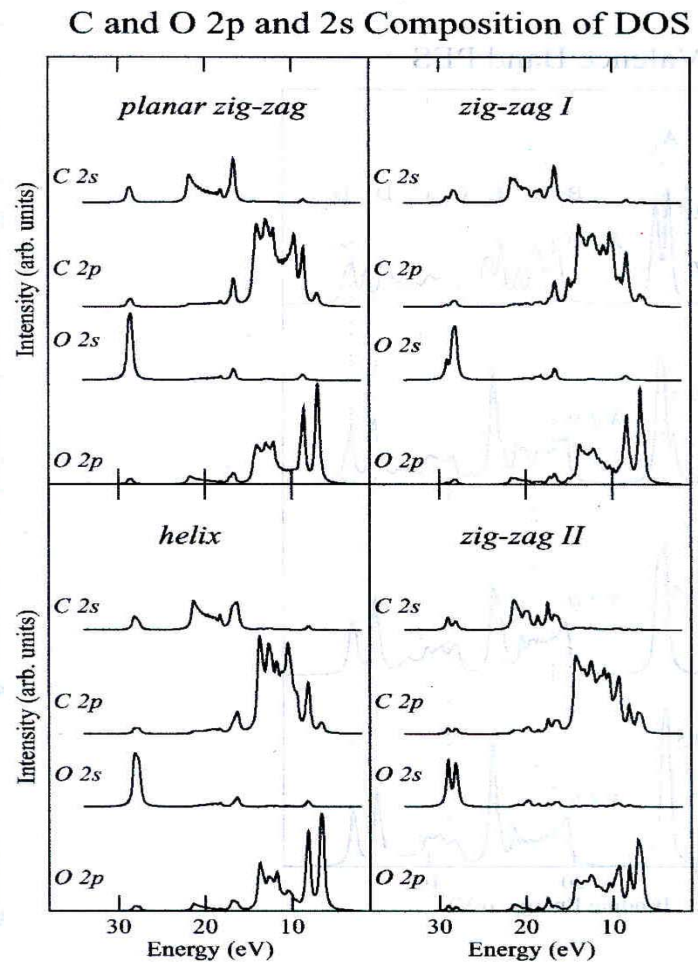
- ❖Delocalized states revealed by XAS calculation
- ❖Fail of building block model, bond-bond interaction is important
- ❖Parallel calculation on lithium oxalate on going to gain more insights

Conformation Dependence of Electronic Structure in Poly (Ethylene Oxide) (PEO)



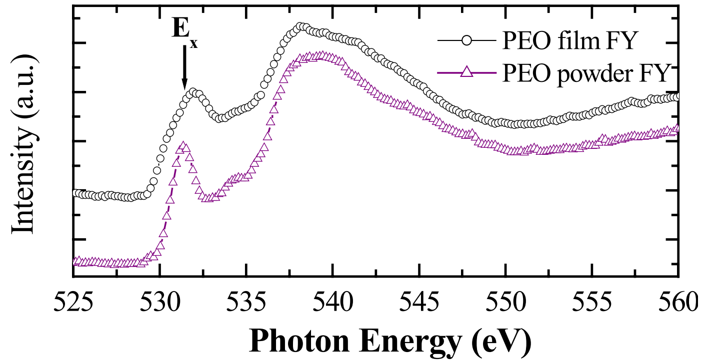
Planer Zig-zag | helix | Zig-zag I | Zig-zag II

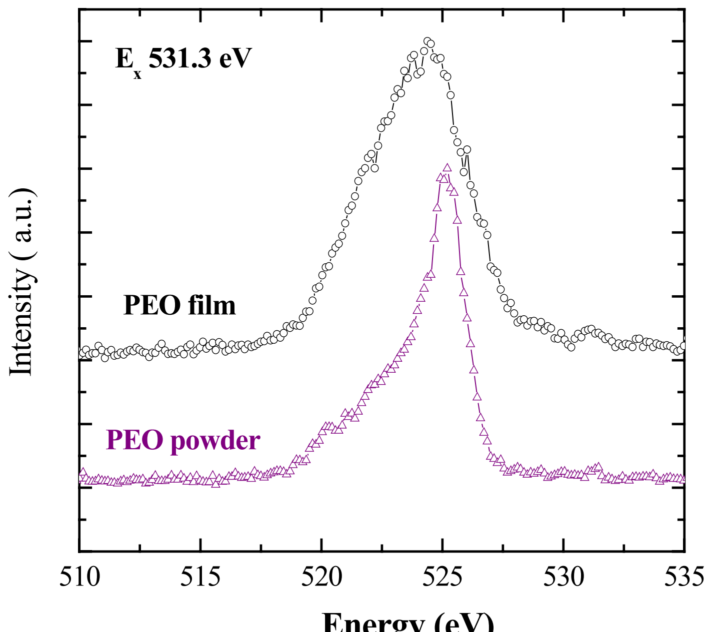


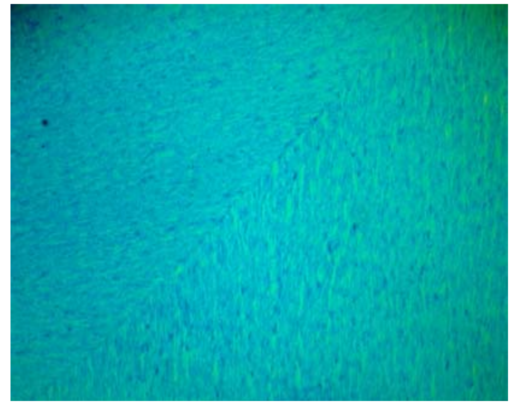


Internal dipole induced by polymer folding has significant effect on Li^+ solvation

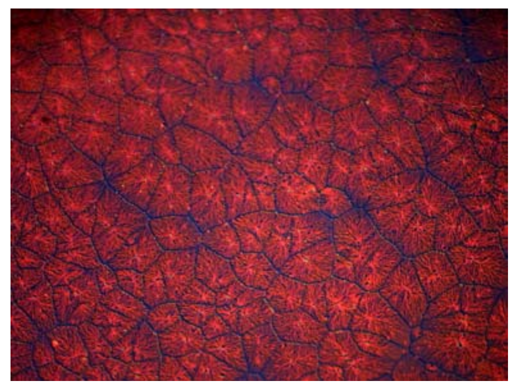
Experimental Electronic Structure (partial DOS) of PEO







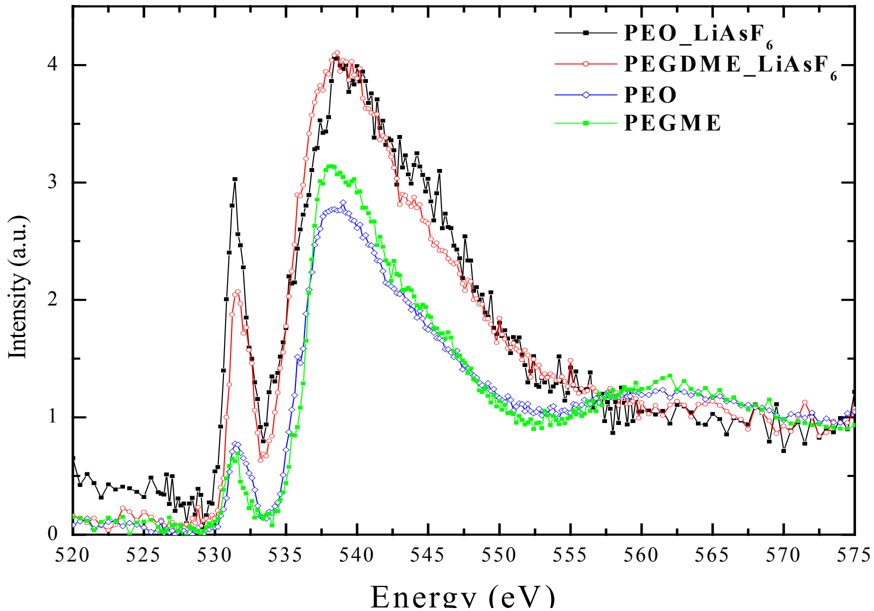
PEO film (Mt. 2000, n≅45)

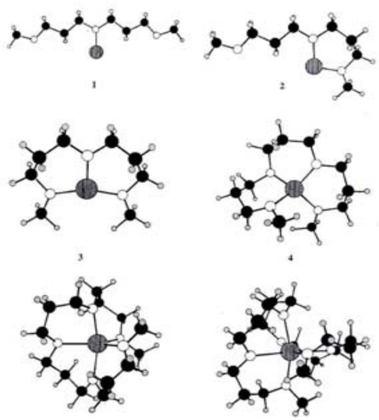


PEO film
(Mt. 600,000 n≅14,000)

Does not limited to crystalline phase, but also amorphous

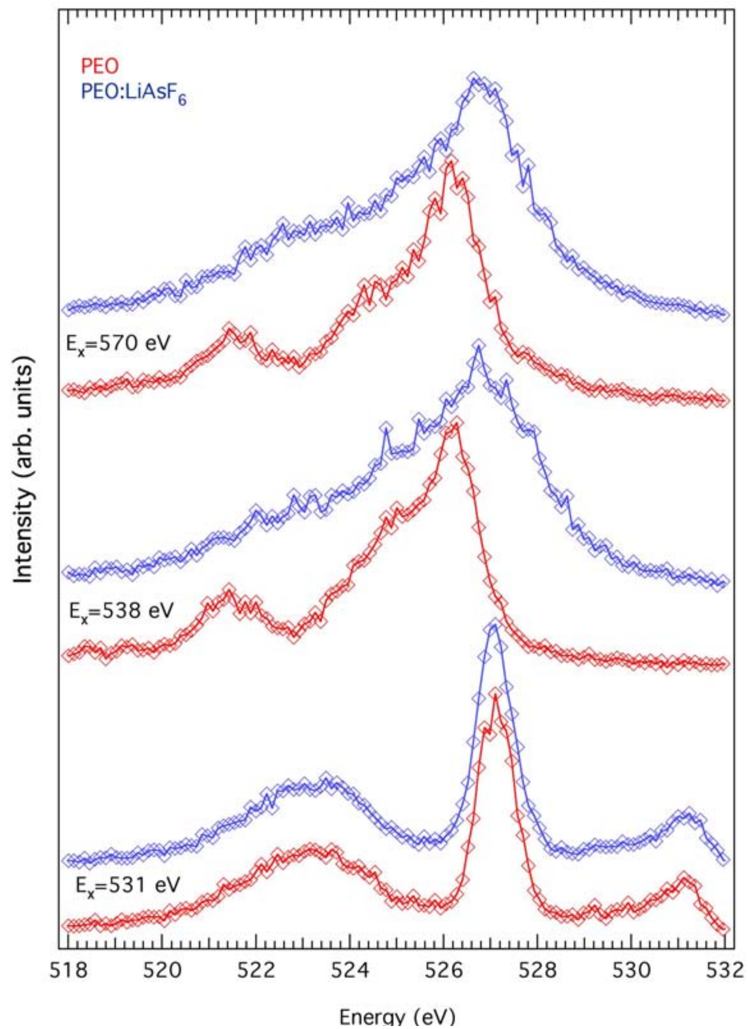
Oxygen XAS and XES of PEO and PEO-LiX:





XAS and XES are sensitive to the polymer conformation and Li-ion solvation

Ref. P. C. Redfern, L.A. Curtiss, J. Power Sources, 110, 401 (2002)



Conclusions and Future Work

➢Current theory is adequate to study carbon and oxygen chemistry, and localized chemical bonding within the anion in crystalline phase of lithium salt.

➢Delocalized bonding in Lithium salt –new physics?

➢Extensive computations are needed to interpret experimental results — finger prints methodology is not sufficient .

➢XAS and XES sensitive to the ion solvation, inter-molecular interaction at short range. Advantages in studying ion-solvation and ion-pairing in amorphous phase as well as in crystalline phase.

➢Resonant XES as a unique tool holds potential for studying complex system in electrochemistry.

➢Exploratory work on Li K-edge emission and Li 1s XAS.